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A new cubic \textit{Ia\textbar{3}d} crystal structure observed in a model single component system by molecular dynamics simulation

Abstract: In our molecular dynamics simulations of the system of identical particles interacting through the harmonic-repulsive pair potential, we observed the formation of a cubic crystal structure that belongs to the \textit{Ia\textbar{3}d} (#230) crystallographic space group. This crystal structure has not been previously seen either in experiments or in computer simulations, though its framework topology has been known from theoretical crystallographic considerations. Its unit cell contains 16 atoms, occupying only (16b) Wyckoff site, and arranged as two mutually intertwined unconnected networks with packing fraction of 0.37. The appearance of this structure is explained by the soft repulsive nature of the interaction potential. The observed \textit{Ia\textbar{3}d} structure extends the small number of cubic structures formed in single component systems with spherically symmetric pair potentials in MD simulations. We speculate that materials with such structure could be found in soft matter systems or in selected crystals under high pressure.

Keywords: cubic; intertwined network; molecular dynamics; monoatomic; single component.

Among the large variety of single particle structures known, there are only about 20 that belong to cubic symmetry. The absolute majority of cubic crystals established experimentally or in computer simulations belong to either face-centered cubic (\textit{fcc}) or body-centered cubic (\textit{bcc}) structures [1]. Examples of less prevalent elementary cubic structures include \textit{\alpha}-Po (simple cubic, cP1), diamond (cF8), \textit{\beta}-W (cP8), \textit{\alpha}-Mn (cI58), \textit{\beta}-Mn (cP20), \textit{\alpha}-N\textsubscript{2} (cP8), \textit{\beta}-O\textsubscript{2} (cP16), etc. Development of high pressure crystallography allowed a number of unique cubic structures for Si, Ga, N and Li to be found [2–5]. New elementary cubic structures have been predicted in simulations under extreme conditions [6, 7]. Also, unusual structures with cubic symmetry have been observed in soft matter systems [8–12]. Here we report the finding of a new cubic structure formed in molecular dynamics simulations in a system of identical particles interacting through the harmonic-repulsive pair potential, initially adopted for soft matter [13–16].

Over the last 30 years significant attention has been paid to modeling of soft matter systems [13, 17–22]. Some soft matter systems consist of star polymers, dendrimers, micelles or microgels in solutions. These mesoscopic particles are approximately spherical in shape, and they can be modeled with spherically symmetric pair potentials [13, 18–23]. In particular, it has been suggested that behavior of some of the mentioned systems can be modeled using the harmonic-repulsive pair potential,

\[ \varphi(r) = \varepsilon(1-r/\sigma)^2 \theta(1-r/\sigma), \]

where \( \theta(x) \) is the Heaviside step function, while \( \varepsilon \) and \( \sigma \) determine the energy and length scales of the potential [12–16].

We performed molecular dynamics (MD) simulations of the single component system of particles interacting through potential (1) under constant volume, with temperature measured in the units of \( \varepsilon \), and distance – in the units of \( \sigma \). Information concerning the details of our MD simulations is presented in Supporting Information. We were initially interested in addressing the generality of several observations described in Refs. [24]. Therefore, using MD simulations we studied the behavior of the system at density of \( \rho \sigma^3 = 3.352 \). At temperature \( T/\varepsilon = 3.75 \times 10^3 \), we observed crystallization into the structure whose pair density function (PDF), after cooling to nearly zero temperature, is shown in Figure 1 with the red curve.

Visual analysis of particles’ configurations in the formed defected crystalline phase has shown presence...
A new monoatomic cubic $\text{La}_3d$ crystal structure of a complex order obscured by many defects. Nevertheless, careful analysis of the repeated structural fragments allowed us to propose a model of the crystal structure, which was initially classified in space group $P\overline{3}21$ ($\#150$). The final crystallographic symmetry of the structure was identified with Findsym [25] software. Running Findsym with the input of atomic coordinates in space group $\#150$ with moderate values of the “tolerance” parameter, yielded the cubic $\text{La}_3d$ (space group $\#230$) solution, of which space group $\#150$ is a subgroup [26].

Validity of the structural solution was confirmed by running MD simulations starting from the proposed structure without defects. The proposed structure was found to be stable at low temperatures and upon heating to the melting temperature of $T/\varepsilon = 10.0 \times 10^{-3}$. Also, the PDF obtained by running MD simulations on the $\text{La}_3d$ structure was compared to the one obtained for the structure formed from liquid (Figure 1). Good agreement between both PDFs supports the correctness of the structural solution.

A crystallographic model of the obtained structure is shown in Figure 2. The structure belongs to space group $\text{La}_3d$ ($\#230$) and has a relatively large unit cell of $a/\sigma = 1.6837$, which is almost three times larger than the shortest interparticle distance. The unit cell of the structure contains 16 particles occupying the $16b$ Wyckoff site only; the independent particle coordinate is $(1/8, 1/8, 1/8)$.

Considering just the shortest interparticle distances, the structure can be represented as two three-dimensional mutually interwoven unconnected networks.

To the best of our knowledge, this crystal structure has not been previously observed either in experiments or in computer simulations. However, the topology of the structure is known from the works in theoretical crystallography, where all possible 3-dimensional networks have been considered and classified [27–30]. It is listed in the International Tables for Crystallography as a lattice complex $Y^{\prime\prime}$ [31]. The $Y^{\prime\prime}$ lattice complex, in turn, can be considered as two intergrown enantiomorphic frameworks, $Y$ and $-Y$, with the net symmetry $I4_132$ and Wyckoff sites $8a$ $(1/8, 1/8, 1/8)$ and $8b$ $(7/8, 7/8, 7/8)$, for the two chiral forms, respectively. The $Y'$ lattice structure is known as silicon sublattice in SrSi$_2$. In the Fischer’s notations of sphere packing frameworks $Y'$, and consequently $Y^{\prime\prime}$, lattices belong to type $3/10/c1$, i.e. all particles are three-connected, forming the smallest ring/mesh of 10 particles and crystallizing in cubic symmetry [28].

Fig. 1: The pair density functions (PDFs) calculated for the structure obtained through crystallization from the liquid phase with a consequent cooling to nearly zero temperature (red) and for the proposed $\text{La}_3d$ crystal structure (blue). Both PDFs clearly show identical peak positions. The larger peak widths at lower temperature in the structure obtained from the liquid phase are caused by structural defects.

Fig. 2: Particles arrangement in the cubic $\text{La}_3d$ structure: (a) within unit cell, (b) along $4_1$-axis, (c) along 3-fold axis. Unit cell borders are shown by grey lines; yellow lines represent the shortest interparticle distances.
The Y\textsuperscript{+} framework has been previously observed in soft matter systems with rod-like molecules, namely in some lipid (soap) – water systems [8–12] and in liquid crystals [8, 32, 33]. In these systems the rod-like molecules form the identical framework but they are arranged in-between of the 16b positions, i.e. along the shortest bonds of the discussed structure.

In the determined Ia\textbar 3d structure all particles have identical neighbor environments shown in Figure 3. Selected parameters, including the interparticle distances for the first four nearest neighbor shells of the structure, are listed in Table 1. The distances to the 2nd, 3rd, and 4th order neighbors are 24%, 60% and 75% larger than the distance to the 1st nearest neighbors. The first nearest neighbor shell of each particle in the networks has a symmetric 3-fold coordination with the shortest bonds oriented along 2-fold axes. The two second-nearest neighbors lie on the 3-fold axis, normal to the first nearest neighbor plane, thus forming infinite straight columns of equally spaced particles. The first and the second nearest neighbors form a stretched trigonal bipyramidal coordination around every particle in the columns.

In the observed Ia\textbar 3d crystal structure, with the given harmonic repulsive potential, the central particle has significant interaction energy with the first, second and third nearest neighbor shells, i.e. ~72%, ~22% and ~6% of the total interaction energy, respectively (Table 1). This observation, in our view, provides an intuitive hint for understanding the appearance of such an unusual structure in the single component system. We believe that formation of this structure became possible because of the combination of particles density and the softness of the potential. It is due to the softness of the potential that interaction energies with the second and the third nearest neighbor shells are unusually high. In contrast, spherically symmetric pair potentials used to model atomic systems generally have a strong repulsive core. For this reason in systems with strong repulsion, interaction with the first neighbor shells prevails and defines the formed structures, typically fcc or bcc.

In our simulations the Ia\textbar 3d structure is formed at densities higher than those at which fcc and bcc structures were found to be stable [14, 15]. We propose that with the decrease of average interparticle distance, lower potential energy for the Ia\textbar 3d phase compared to the fcc and bcc structures is achieved because the interaction with a wider range of nearest neighbor shells becomes significant for this topology, in contrast to simpler bcc and fcc ones. In fact, at density $\rho_o \sigma^3 = 3.352$, the fractions of calculated interaction energy with the 1st, 2nd and 3rd nearest neighbor shells for hypothetical fcc and bcc structures correspond to: 100%, 0%, 0% for fcc and 80%, 20%, 0% for bcc, respectively.

Formation of more complex and open structures with soft or soft tail isotropic potentials compared to hard core potentials have been demonstrated before [18, 20, 34]. Regarding cubic structures, it was shown that while in hard repulsive potentials only simple cubic, fcc and bcc normally form, utilizing soft potentials allows crystallization of a larger number of cubic structures. In particular,
diamond and β-W (known in two-atomic systems as A-15) structures have been observed [18, 34]. Thus, the discovered \( Ia\overline{3}d \) structure extends the small number of cubic structures found in single component systems with simple spherically symmetric pair potentials in MD simulations. In our view, it is quite remarkable that such a complex structure forms for such simple interactions, as interaction (1).

This situation resembles the formation of complex magnetic structures in a system with competing (bilinear) exchange interactions, which is discussed in particular in Ref. [35]. When only the nearest neighbors are relevant, there occur simpler structures: ferro- or antiferromagnetic. However, if further neighbors become relevant, more complex magnetic structures are formed.

The calculated atomic packing factor for the structure is equal to 0.370 which is significantly smaller than that for \( fcc \) (0.74), \( bcc \) (0.68), and most other monatomic cubic structures; but rather close to one in diamond (0.34), which is also a framework structure.

The \( Ia\overline{3}d \) structure is expected to be found in soft matter systems for which the interaction potential used in our MD simulation was initially adopted. Given the harmonic repulsive nature of the potential, we can suggest that, the observed structural motif could also be found in atomic or molecular crystals especially under pressure which favors the repulsive interaction over the attractive interaction. This situation could be expected to occur in phases containing 3- or 5-valent atoms forming trigonal bipyramidal atomic arrangement, similar to the first and the second nearest neighbor coordination of the \( Ia\overline{3}d \) structure.

For instance, the found structure could be adopted for phosphorus or nitrogen under extreme conditions. So far the only form of polymerized nitrogen was found to crystallize in the so called cubic gauche structure (cgN, space group \( I\overline{2}\overline{1}3 \)) [5]. In cgN all nitrogen atoms have three neighbors forming a framework similar to the single framework in the \( Ia\overline{3}d \) structure (\( Y' \)). The cgN, as well as \( Y' \), belongs to the same type \( 3\overline{1}0/c1 \) by Fischer’s classification [28], but differs in bond (\(-114^\circ\)) and dihedral angles (\(-107^\circ\)), which are equal 120° in the \( Y' \) framework. The packing fraction of the cgN structure is equal 0.25 [5]. We can speculate that having a higher packing fraction of 0.37, the \( Ia\overline{3}d \) structure could be found in nitrogen at higher pressures and temperatures.

The phase diagram of the particles interacting through the harmonic-repulsive pair potential has been investigated in Ref. [14]. As far as we understand, the analysis presented in Ref. [14] was based on initial assumptions with respect to possible crystal structures. The possibility of formation of the \( Ia\overline{3}d \) crystal structure has not been assumed and thus conclusions that had been made do not correctly describe the behavior of the system at the studied value of the density. Phase formation in the system at various densities is planned to be completed and reported later by V.A.L. in a follow-up publication.

**Supplementary information**

We performed molecular dynamics simulations (MD) using the LAMMPS program [36]. The simulations were performed using the Lennard-Jones (LJ) units [http://lammps.sandia.gov/doc/units.html]. This choice of units determines the energy scale: if the value of the harmonic-repulsive potential (1) at zero separation is equal to one, i.e. \( \varepsilon = 1 \), then \( \varepsilon \) corresponds to the depth of the minimum of the LJ-potential in the LJ-units. If the length scale of the harmonic repulsive potential is equal to one, i.e. \( \sigma = 1 \), then this length corresponds to the particles’ diameter of the LJ-potential in the LJ-units. In MD simulations we measured temperature, \( T \), in the units of \( \varepsilon \) and time, \( t \), in the units of \( \tau = \sqrt{\sigma^2 m/\varepsilon} \), in accordance with the LAMMPS conventions [http://lammps.sandia.gov/doc/units.html]. The magnitude of the time step was determined in the constant energy runs (NVE-ensemble) so that the total energy of the system is conserved with high precision (essentially no variation in the sixth digit of the value of the total energy per particle). The data were acquired in the constant temperature runs (NVT-ensemble) with Nosé-Hoover thermostat. The value of the time step varied in the interval between \( \delta t \approx 0.001 \) for high temperatures \((T/\varepsilon) \approx 0.015 \) and \( \delta t \approx 0.1 \) for nearly zero temperature \((T/\varepsilon) \approx 0.000025 \). The value of the dumping parameter associated with the Nosé-Hoover thermostat was chosen to be equal to approximately 100 time steps. Our simulations were performed on the systems containing 13,500, 16,000, and more than 100,000 particles in a cubic simulation box. The periodic boundary conditions were always assumed. In our simulations we did not notice size effects. Correspondingly, we do not mention the size of the system on which the data were obtained.

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References

[1] According to the Inorganic Crystal Structure Database (https://icsd.fizkarlsruhe.de) by 2016 there were 855 single element cubic structure entries, 405 of which were fcc and 269 – bcc.


Graphical synopsis

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